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FORM PTO-1390 (Modified)  
REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

**UOGR-009-US**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

Not Yet Assigned 09 / 806790

INTERNATIONAL APPLICATION NO  
PCT/GB99/03318

INTERNATIONAL FILING DATE  
**7 October 1999**

PRIORITY DATE CLAIMED  
7 October 1998

**TITLE OF INVENTION**

## MEMBRANE STRUCTURE

APPLICANT(S) FOR DO/EO/US

Bratton et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

**Items 13 to 20 below concern document(s) or information included:**

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

### Written Opinion

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) <b>Not Yet Assigned</b> <span style="font-size: 1.5em; font-weight: bold;">09/806790</span>	INTERNATIONAL APPLICATION NO. <b>PCT/GB99/03318</b>	ATTORNEY'S DOCKET NUMBER <b>UOGR-009-US</b>
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21. The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :**

- |  |          |
|--|----------|
| <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... | \$970.00 |
| <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .....  | \$840.00 |
| <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....  | \$690.00 |
| <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....   | \$670.00 |
| <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) .....   | \$96.00  |

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

**CALCULATIONS PTO USE ONLY**

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

\$860.00

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	11 - 20 =	0	x \$18.00	\$0.00	
Independent claims	2 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable).				<input type="checkbox"/>	\$0.00
<b>TOTAL OF ABOVE CALCULATIONS</b>				<b>=</b>	<b>\$860.00</b>

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☒

**SUBTOTAL =**

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

**TOTAL NATIONAL FEE =**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☒

**TOTAL FEES ENCLOSED =**

	Amount to be:	\$
	refunded	
	charged	\$

☐ A check in the amount of \_\_\_\_\_ to cover the above fees is enclosed.

☒ Please charge my Deposit Account No. **50-0765** in the amount of \_\_\_\_\_ to cover the above fees.

A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment

to Deposit Account No. **50-0765** A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

Ronald B. Sherer  
Bartlett & Sherer  
103 South Shaffer Drive  
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Ronald B. Sherer  
SIGNATURE

Ronald B. Sherer  
NAME

19,977  
REGISTRATION NUMBER

19,977  
REGISTRATION NUMBER

19,977  
REGISTRATION NUMBER

2 APRIL 01  
DATE

70

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS (37 CFR 1.9(f) AND 1.27 (b)) - INDEPENDENT INVENTOR

UDGR-9-US

Serial No. <i>NOT YET ASSIGNED</i>	Filing Date <i>HEREWITH</i>	Patent No. <i>N/A</i>	Issue Date <i>N/A</i>
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Applicant/  
Patented: — *BRATTON ET AL* —

Invention:  
*MEMBRANE STRUCTURE*

As a below named inventor, I hereby declare that I qualify as an independent inventor as defined in 37 CFR 1.9(c) for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, to the Patent and Trademark Office with regard to the invention entitled above and described in:

- ☒ the specification to be filed herewith.
- ☐ the application identified above.
- ☐ the patent identified above.

I have not assigned, granted, conveyed or licensed and am under no obligation under contract or law to assign, grant, convey or license, any rights in the invention to any person who could not be classified as an independent inventor under 37 CFR 1.9(c) if that person had made the invention, or to any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

- ☐ No such person, concern or organization exists.
- ☒ Each such person, concern or organization is listed below.

\*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities (37 CFR 1.27)

FULL NAME — *SMART (ILE OF MAN) LIMITED*

ADDRESS *45 VICTORIA ST., DOUGLAS, UK IM1 2LD*

☐ Individual ☒ Small Business Concern ☐ Nonprofit Organization

FULL NAME  
ADDRESS

☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME  
ADDRESS

☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME  
ADDRESS

☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF INVENTOR GRAHAM J. BRATTON

SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: 29 MAR. 01

NAME OF INVENTOR KARAN D. BUCK

SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: 29 MAR. 01

NAME OF INVENTOR TIMOTHY D.V. NAYLOR

SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: 29 MAR. 01

NAME OF INVENTOR MARTIN G. MAJOR

SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: 29 MAR. 01

NAME OF INVENTOR \_\_\_\_\_

SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: \_\_\_\_\_

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SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: \_\_\_\_\_

NAME OF INVENTOR \_\_\_\_\_

SIGNATURE OF INVENTOR \_\_\_\_\_

DATE: \_\_\_\_\_

09/806790

JCO8 Rec'd PCT/PTO 02 APR 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PCT GROUP

Applicant(s): ) Title: MEMBRANE STRUCTURE  
Bratton et al )  
U.S. Serial No: Not Yet Assigned ) Art Unit: Unknown  
International Application No.: ) Examiner: Unknown  
PCT/GB99/03318 ) Attorney Docket:  
International Filing Date: ) UOGR-009-US  
7 October 1999 )  
U.S. Filing Date: ) I hereby certify that this  
Filed Herewith ) correspondence is being deposited with  
the United States Postal Service as  
first class mail in an envelope  
addressed to: Assistant Commissioner  
for Patents, Washington, D.C. 20231  
on 2 APRIL 01

FIRST PRELIMINARY AMENDMENT

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

Sir:

Please amend the above-identified International (PCT)  
Application, which is filed herewith, as follows:

In order to reduce the filing fee, and also improve the form  
of the claims and thereby expedite the prosecution, please cancel  
Claims 1 - 15 and substitute new Claims 16 - 26 as follows:

16. A membrane structure comprising a tubular porous ceramic monolith support which has an average pore size of 1 to 20 microns having at least four tubular conduits formed within the monolith with a zeolite membrane formed on the internal surface of the conduits, the zeolite membrane having an internal diameter of 5 to 9 millimetres and the ceramic monolith having an outer diameter of 20 to 25 millimetres.

17. A structure as claimed in claim 16 in which the zeolite membrane has a diameter of 6.4 millimetres.

18. A structure as claimed in claim 16 in which the ceramic monolith has an outer diameter of 20mm.

19. A structure as claimed in claim 16 in which the porous ceramic monolith is formed of a sintered ceramic powder of alpha alumina, titania or zirconia.

20. A membrane structure comprising a tubular porous ceramic monolith support which has an average pore size of 1 to 20 microns having at least four tubular conduits formed within the monolith with a zeolite membrane formed on the internal surface of the conduits, the zeolite membranes having an internal diameter of 5 to 9 millimetres and the ceramic monolith having an outer diameter of 20 to 25 millimetres, in which the zeolite membrane is formed by a process which comprises deposition or crystallisation from a growth medium onto the ceramic monolith.

21. A membrane structure as claimed in claim 20 in which the porous support is contacted with the growth medium by contacting the inner surface of the tubular conduits with the growth medium.

22. A membrane structure as claimed in claim 21 in which the porous support is pre-treated with a zeolite initiating agent.

23. A membrane structure as claimed in claim 20 in which the porous support is pre-treated with a zeolite initiating agent selected from a cobalt, molybdenum or nickel oxide or particles of a zeolite.

24. A membrane structure as claimed in claim 20 in which the porous support is pre-treated with a zeolite initiating agent selected from silicic acid or polysilicic acid.

25. A membrane structure as claimed in claim 20 in which the porous support is pre-treated with a zeolite initiating agent by a process in which a liquid suspension of a powder of the zeolite initiation agent is formed and the liquid suspension contacted with the porous support to deposit the zeolite initiation agent on the support and in which the porous support is then contacted with the growth medium by contacting the inner surface of the tubular conduits with the growth medium and after formation, the membrane is treated with a surface modifying agent which cross links with the zeolite membrane to form a membrane with substantially no defects.

26. A membrane structure as claimed in claim 25 in which, after formation, the membrane is treated with a surface modifying agent which cross links with the zeolite membrane to form a membrane with substantially no defects is selected from silicic acid or an alkyl silicate.

The claims have been reduced in number in order to reduce any issues and thereby assist the Examiner.

Respectfully submitted,

*Ronald B. Sherer*

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Membrane Structure

5 The present invention relates to a membrane structure with improved performance characteristics which is particularly useful for zeolite membranes.

10 A commonly used membrane structure for separating two components consists of a tubular membrane with the mixture being passed down the tube and a separated component passing through the membrane and the other component or mixture of components passing down the tube. The tube can be bent so that it is in the form of a continuous zig-zag or other convoluted or similar configuration to increase the surface area of the tube contained in a module.

15 Alternatively or in addition there can be a plurality of tubes arranged substantially in parallel to increase the surface area of membrane without having too large a diameter of each tube or tube length.

20 In a module for use in separation or filtration processes using tubular membranes, the size and configuration of the membranes is chosen so that the optimum performance can be achieved. For a tubular membrane, the larger the diameter of the tube the greater the surface area per unit length of the tube and the lower the pressure drop down the tube, this is normally a desired criterion. However the larger the diameter of the tube, the greater the possibility, at any given flow rate of streamline flow down the tube and the greater the distance from the centre of the tube to the membrane and these will lead to a corresponding loss of performance. Whereas a narrower tube gives a lower surface area per unit length, and requires a lower flow rate to give the same degree of turbulence, but gives a higher pressure drop. In order to balance these characteristics, a series of parallel tubes in a module can be used, with the diameter of each tube chosen for optimum performance and the number of tubes chosen to have  
30 the desired surface area in the module.

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5 With ceramic membranes it is cost efficient and convenient to form a plurality of tubes together in the form of a monolith. Hence monolithic assemblies of tubes have been developed wherein a single, tubular body comprises a multiplicity of smaller channels.

10 The number and shape of the inner channels can vary. For example, monoliths with 7, 19 or a greater number of channels have been developed as well as monoliths with star or other shaped channels. Typically, such designs have been developed so as to maximise the surface area per unit length of monolith, combined with minimum pressure drop whilst maintaining high overall permeability.

15 We have found that a particular arrangement of tubular membranes gives unexpectedly superior results for zeolite membranes in pervaporation over what would have been expected.

20 According to the invention there is provided a comprising a tubular porous ceramic monolith having at least four tubular conduits formed within the monolith with a zeolite membrane formed on the internal surface of the conduits the zeolite membranes having an internal diameter of 5 to 9 millimetres preferably 6.4 millimetres and the ceramic monolith having an outer diameter of 20 to 25 millimetres, preferably 20mm.

25 In practice the internal diameter will vary along the length of the tubular membrane and will vary according to membrane thickness, so the internal diameter of the tubular membranes is an approximate average along the length of the tube and the invention will encompass structures which deviate from the exact measurements in accordance with normal practice.

- 3 -

The length of the porous ceramic monolith will depend on the use to which the zeolite membrane is to be used and the vessel into which it is to be fitted. In general lengths of from 1 to 10 metres are useful in many applications.

- 5 The tubular zeolite membrane is preferably formed by the methods disclosed in our co-pending patent applications PCT/GB96/00243, PCT/GB97/00928 and PCT/GB 97/00635.

- 10 Typical zeolites which can be used in the present invention include but are not limited to, 3A, 4A, 5A, 13X, X, Y, ZSM5, MPOs, SAPOs, Silicalite, etc.

- 15 The porous supports on which zeolite membranes are formed are preferably formed of sintered ceramic powders such as alpha alumina, titania, zirconia or other suitable media which are capable of being extruded and sintered upon which the zeolite will nucleate and grow.

- 20 The present invention can be used with porous supports of any suitable size although, for large flux rates through a membrane, large pore sizes are preferred. Preferably pore sizes of 0.01 to 2,000 microns, more preferably of 0.1 to 200 and ideally of 0.1 to 20 microns are used. Pore sizes up to 300 microns can be determined by bubble point pressure as specified in ISO 4003. Larger pore sizes can be measured by microscopic methods.

- 25 The membranes which can be used in the present invention can be formed by any method, for example by crystallisation from a gel or solution, by plasma deposition or by any other method such as electro-deposition of crystals on conducting substrates e.g. as described in DE 4109037.

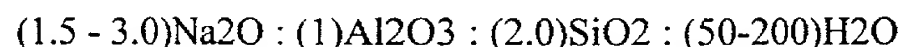
- 4 -

When the membrane comprising a film of a zeolite material is prepared by crystallisation from a synthesis gel, any of the methods described in the prior art can be used.

- 5 The synthesis gel used in the process can be any gel which is capable of producing the desired crystalline zeolite membrane. Gels for the synthesis of zeo-type materials are well known and are described in the prior art given above or, for example, in EP-A-57049, EP-A-104800, EP-A-2899 and EP-A-2900. Standard text books by D W Breck ("Zeolites Molecular Sieves, Structure Chemistry and Use") published by John Wiley (1974) and P.A Jacobs and J.A Martens (Studies in Surface Science and Catalysis No. 33, Synthesis of High Silica Alumino silicate Zeolites" published by Elsevier (1987), describe many such synthesis gels. The process which can be used includes conventional syntheses of zeolite membranes, except that the synthesis is carried out in the presence of the porous support. Most commonly, gels are crystallised by the application of heat.

The membrane can be prepared by a process which comprises deposition or crystallisation from a growth medium. One method for forming the membrane preferably has a molar composition in the range of

20



and the method used can be used in any of the methods disclosed in the references listed above

- 25 The conditions which can be used for forming the membrane are with a temperature of the growth solution preferably in the range of 50 to 100°C and the pH can be adjusted e.g. to pH of 12.5 to 14 by addition of sodium hydroxide or ammonia. If desired the sodium ion concentration can be increased without increasing the pH by the addition of a sodium salt such as sodium chloride. The growth solution can be

- 5 -

seeded with zeolite crystals of the desired zeolite to be synthesised. The membrane can be washed to pH neutral after membrane formation prior to any post-treatment.

5 The porous support can be contacted with the growth medium by immersion or by pouring the growth medium over the support with the support held substantially horizontal, either face up at the bottom of a container, or face down at the surface of the growth medium, or it can be passed over one or both sides of the support, with the support held substantially horizontal, or it can be passed over one or both sides of the support with the support held substantially vertical or the support can be in any  
10 intermediate position.

The growth medium can be kept static, stirred, tumbled or passed over or around the support, alternatively the growth medium can be passed over both sides of the support with the support held substantially horizontal or at any intermediate position.

15 Pressure may also be applied but it is usually convenient to conduct the crystallisation under autogenous pressure. Preferably the porous support is completely immersed in the growth medium; alternatively, if desired, only one surface of the support may be in contact with the growth medium. This may be useful, for example,  
20 if it is desired to produce a membrane in the form of a tube, where only the inside or outside of the tube need be in contact with the growth medium.

It may be useful if it is desired to produce a membrane containing two different zeolites, one on each side of the support. Use of such a bi-functional membrane  
25 would be equivalent to using two separate membranes, each carrying a different zeolite.

If desired, the treatment with the gel can be repeated one or more times to obtain thicker membrane coatings.

30

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Preferably the porous support is pre-treated with a zeolite initiating agent. The zeolite initiating agent is preferably a cobalt, molybdenum or nickel oxide or it can be particles of a zeolite, e.g. the zeolite which it is intended to deposit on the porous support, or any combination of these. Another example of an initiating agent is a compound which can deposit a zeo-type pre-cursor material e.g. a silicic acid or polysilicic acid.

10 The zeolite initiation agent can be contacted with the porous support by a wet or dry process. If a dry process is used, the particles of the zeolite initiation agent can be rubbed into the surface of the porous material, or the porous material surface can be rubbed in the particles.

15 Alternatively the particles of the zeolite initiation agent can be caused to flow over and/or through the porous support, or pulled into the support by means of a vacuum.

If a wet process is used, a liquid suspension of powder of the zeolite initiation agent is formed and the liquid suspension contacted with the porous support to deposit the zeolite initiation agent on the support.

20 Before contacting the surface of the porous support with the zeolite initiation agent the surface is preferably wetted with wetting agent such as an alcohol, water or a mixture of these.

25 After formation the membrane is preferably treated with a surface modifying agent which can cross link with the zeolite membrane and thus form a membrane with substantially no defects. The preferred surface modifying agents are silicic acid and silicates such as alkyl silicates e.g. tetra ethyl orthosilicate (TEOS).

30 In the present specification by silicic acid is meant monosilicic, low, medium and high molecular weight polysilicic acids and mixtures thereof.

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Methods of making silicic acids are described in GB Patent Application 2269377.

5 The silicic acids used can have a "narrow" molecular weight distribution as formed or in a combination of different molecular weight ranges.

Greater flexibility can be introduced into the final membranes by treating them with a flexibilising agent by adding e.g. a hydroxy terminated polysiloxane into the silicic acid solution before treatment of the membrane.

10

The membrane structures of the present invention can be used in a range of separation and catalytic processes, e.g. dehydration of LPG, air, alcohols and natural gas, removing linear alkanes, olefins and substituted hydrocarbons from mixtures with branched chain compounds, e.g. in reforming, dewaxing, etc., hydrogenation and

15

The invention is described in the Example.

20 Example

A ceramic substrate of the structure of fig.1 of the drawing was pre-treated so as to deposit zeolite 4A powder on the inside of the channels using the following method.

25 The outer ceramic tube (1) had a diameter of 20mm and the inner tubes (2) had a diameter 6.4mm

An appropriate sized pipe cleaner, which had been loaded with zeolite 4A particles (nominally sized 2-5µm) was inserted into one channel of a porous ceramic tube 60

30 cm long by 20 mm overall diameter with four channels each 6.4mm diameter and fed

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through the bore of one channel until it emerged out of the other end (the pipe cleaner was twisted to form a stiffer rod so as to aid insertion through the tube). The pipe cleaner was pulled backwards and forwards through the channel effecting a deposit of 4A particles on the internal walls of the channel. This was repeated for each of the remaining three channels.

By this method of powder deposition, between  $0.435 \times 10^{-4}$  and  $2.39 \times 10^{-4}$  g/cm<sup>2</sup> of powder were deposited on the total surface of the ceramic support. The total weight of powder deposited was found to vary with the pore size of the ceramic support.

Membrane growth procedure

The zeolite membrane was formed on the inside of the four pre-treated channels by allowing a hydrogel suspension to be in contact with the surfaces under the conditions described below.

The hydrogel is formed by combining two separate solutions, (solution A) and (solution B) to form a homogeneous suspension.

Solution A

24.49g Sodium Aluminate, 3.75g Sodium Hydroxide and 179.74g de-ionised water were mechanically shaken until dissolved. The Sodium Aluminate had an actual composition 62.48% Al<sub>2</sub>O<sub>3</sub>, 35.24% Na<sub>2</sub>O, and 2.28% H<sub>2</sub>O.

Solution B

50.57g Sodium Silicate of composition 14.21% Na<sub>2</sub>O, 35.59% SiO<sub>2</sub> and 50.20% H<sub>2</sub>O was dissolved in 148.8g de-ionised water.



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Solution A was heated to 50°C and added slowly to solution B which had been pre-heated to 90°C with stirring to ensure complete and even mixing (it is important that no lumps of hydrogel are formed). The mixture was then heated to 95°C. This resulted in a hydrogel having a molar composition

5

2.01 Na<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub>: 2.0 SiO<sub>2</sub> : 143.10 H<sub>2</sub>O

10

The pre-treated tube was wetted by immersing it in deionised water for 15 seconds. The tube was then suspended vertically above the bottom of the growth vessel. Hot hydrogel was then added to the growth vessel, care being taken to ensure that all the air was expelled from the channels .

The growth vessel was sealed and heated to 100°C for 5 hours.

15

After 5 hours the tube was removed from the growth vessel, allowed to cool slightly and then removed and washed clean using deionised water over a period of 16 hours. The ceramic tube was then dried at 100°C for 6 hours.

X-ray Analysis showed this to be a Zeolite 4A.

20

A mixture of polysilicic acids of mean molecular weight of about 800 was diluted with ethanol to 5% wt. solids. 500ml. of this solution was circulated over the feed side of the membrane and drawn through the membrane to treat the surface whilst being heated to 70° C., with vacuum for 5 hours to cross-link the silicic acid in the pores of the membrane.

25

A comparison of the performance of the four channelled monolith with that of a single narrow tube in water separation from a water/isopropanol mixture at 70°C. Care was taken to ensure that the tubes were tested under identical conditions of turbulence of the feed solution and the results shown below.

30

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5	Tube Type	Water Flux	Number of	Tube price per	£/Kg water
		Kg/ m <sup>2</sup> /day	tubes per m <sup>2</sup>	m <sup>2</sup> at £100 each	removed
		At Re8582 and			
		2% wt Water/			
		IPA at 70°C			
	4 Channel	21	22	2200	200
	Narrow bore	41	100	10,000	243.9

10

The tube dimensions were

15		Tube Diameter	Tube Inner	Tube area per
		mm	Circumference	58cm length
			mm	
	4 channel	4 x 6.4	7.92	459
	Narrow Bore	1 x 5.5	1.728	100.2

20

As can be seen the four tube configuration is surprisingly superior in performance and cost per unit area of membrane.

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## Claims

1. A membrane structure comprising a tubular porous ceramic monolith having at least four tubular conduits formed within the monolith with a zeolite membrane  
5 formed on the internal surface of the conduits the zeolite membranes having an internal diameter of 5 to 9 millimetres and the ceramic monolith having an outer diameter of 20 to 25 millimetres.

2. A structure as claimed in claim 1 in which the zeolite membranes have a diameter  
10 of 6.4 millimetres.

3. A structure as claimed in claim 1 or 2 in which the ceramic monolith has an outer diameter of 20mm.

4. A structure as claimed in any one of claims 1 to 3 in which the porous ceramic monolith is formed of a sintered ceramic powder of alpha alumina, titania or zirconia.  
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5. A membrane structure as claimed in any one of claims 1 to 4 in which there are from 4 to 7 tubular conduits  
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6. A membrane structure as claimed in any one of claims 1 to 5 in which the porous support has an average pore size of 0.01 to 2,000 microns

7. A membrane structure as claimed in any one of claims 1 to 5 in which the porous support has an average pore size of 1 to 20 microns.  
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8. A membrane structure as claimed in any one of the preceding claims in which the zeolite membrane is formed by a process which comprises deposition or crystallisation from a growth medium onto the ceramic monolith.  
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- 12 -

9. A membrane structure as claimed in claim 8 in which the porous support is contacted with the growth medium by contacting the inner surface of the tubular conduits with the growth medium.

5 10. A membrane structure as claimed in claim 9 in which the porous support is pre-treated with a zeolite initiating agent.

11. A membrane structure as claimed in claim 10 in which the zeolite initiating agent is a cobalt, molybdenum or nickel oxide or particles of a zeolite.

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12. A membrane structure as claimed in claim 10 in which the zeolite initiating agent is a silicic acid or polysilicic acid.

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13. A membrane structure as claimed in any one of claims 10 to 12 in which the porous ceramic monolith is treated with the zeolite initiating agent by a process in which a liquid suspension of powder of the zeolite initiation agent is formed and the liquid suspension contacted with the porous support to deposit the zeolite initiation agent on the support.

20

14. A membrane structure as claimed in any one of the preceding claims in which after formation the membrane is treated with a surface modifying agent which cross links with the zeolite membrane to form a membrane with substantially no defects.

25

15. A membrane structure as claimed in claim 14 in which the surface modifying agents is silicic acid or an alkyl silicate.

1/1

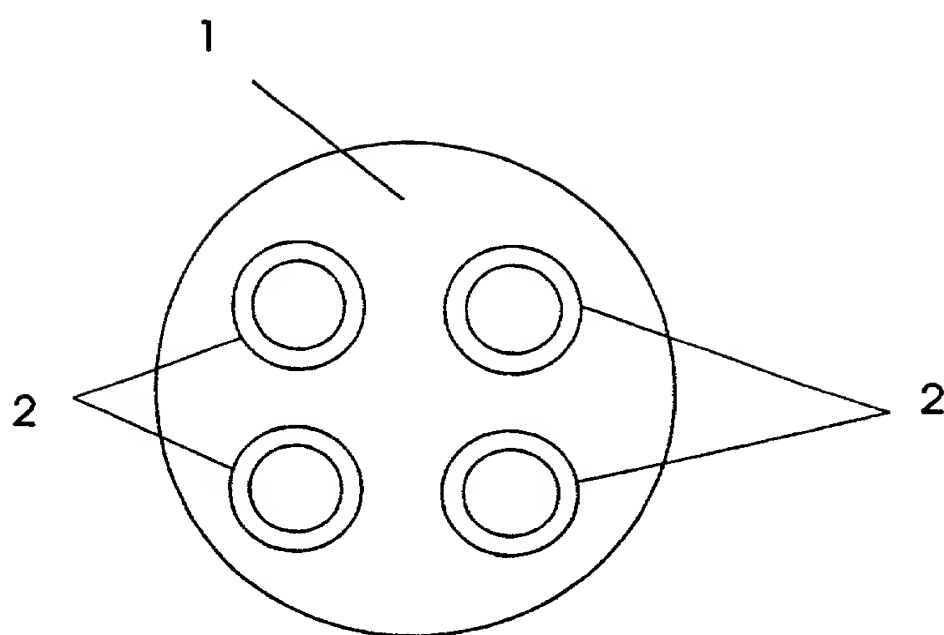


Fig. 1

Docket No.  
UOGR009-US

## Declaration and Power of Attorney For Patent Application

### English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

#### MEMBRANE STRUCTURE

the specification of which

(check one)

☐ is attached hereto.

☐ was filed on 7th October 1999 as United States Application No. or PCT International Application Number PCT/GB99/03318 and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>UK 98 21706.0</u> (Number)	<u>UK</u> (Country)	<u>7th October 1998</u> (Day/Month/Year Filed)	<input type="checkbox"/>
<u>                    </u> (Number)	<u>                    </u> (Country)	<u>                    </u> (Day/Month/Year Filed)	<input type="checkbox"/>
<u>                    </u> (Number)	<u>                    </u> (Country)	<u>                    </u> (Day/Month/Year Filed)	<input type="checkbox"/>

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

**PCT/GB99/03318**

**7th October 1999**

**Pending**

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

\_\_\_\_\_  
(Application Serial No.)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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3-00

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